

# Memorandum

**To:** Eric Blischke and Chip Humphrey, EPA Region 10

From: Lower Willamette Group

CC:

**Date:** January 20, 2010

**Re:** Total PCB Modeling Approach

In EPA's comments on the QEAFATE model dated November 24, 2009, it was requested that the LWG consider modeling total PCBs (tPCB) rather than individual PCB congeners. After further consideration, the LWG notified EPA in a meeting on January 13, 2010 that it will proceed with modeling tPCB. This memo briefly describes the planned approach for this modeling.

### APPROACH FOR MODELING TOTAL PCBS

As presented in the RI, the tPCB composition in surface sediment exhibits variation across the study area, including RMs 2 to 4, and between RMs 6.7 and 11.3 in the eastern nearshore zone (see RI Section 5.1.5.5). Similar variations may exist in deeper sediment and the water column under varying flow conditions. As a result of these spatial differences in composition, directly modeling tPCB would be difficult because (1) it would require a significant effort to develop representative model parameters (e.g., partition coefficients) that reflect the spatial patterns in PCB composition across the site; and (2) the model results may not represent certain locations or conditions very well since this approach would need to assume that the PCB composition does not change over time. (Note that this circumstance differs from many other sites where tPCB is modeled; at these sites there is typically one dominant PCB source that is present, e.g., the Hudson and Fox River sites.) Because of these issues, the LWG proposes modeling select homolog groups as a means of predicting tPCB. The primary advantage of modeling PCB homologs over tPCB directly is that such an approach eliminates the difficulties associated with the "shifting composition" issue identified above.

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The LWG does not believe it is necessary to model all ten PCB homolog groups to provide predictions of tPCB concentrations in the Lower Willamette; rather, analyses will be conducted with site-specific water column, sediment, stormwater, and biota data to identify the subset of PCB homologs that can account for the majority of the PCB mass within the system, across the various media. For example, as noted in the RI, the PCB homolog groups containing four to seven chlorines are the predominant homolog groups in the Study Area sediments (see RI Section 5.1.5.5). In the QEAFATE model, each of the selected homologs would be simulated separately; predictions for these homolog groups would then be summed, and scaled up to provide predictions of tPCB. This scale-up procedure would consist of applying a scale factor or relationship that relates the total concentration of the homolog groups selected for modeling to the total PCB concentration, for both the sediments and water column.

Because tPCB results will be available using the above approach, we no longer propose to model PCB 126 and 77 congeners individually as proposed in previous descriptions of PCB modeling approaches. The tPCB information is expected to be directly usable in the Food Web Modeling in a manner analogous to previously proposed Food Web Modeling for PCBs. Previously proposed modeling of individual 126 and 77 congeners was never expected to result in PCB TEQ estimates (nor is tPCB) for sediment or water in the chemical fate modeling or tissue in the Food Web Modeling.

Development of inputs for the homolog PCB model based on site-specific monitoring data (e.g., sediment initial conditions, water column boundary conditions, stormwater loads) is generally straightforward using the congener data sets; calculation of homologs from congeners simply involves summing the appropriate congeners within each respective homolog group. However, as noted by EPA in its November 24, 2009 comments on the QEAFATE modeling, the spatial coverage of the congener data set is somewhat limited, particularly for subsurface sediments. Therefore, the LWG proposes using the Aroclor-based data set to supplement the congener data. The planned methods for estimating PCB homologs from the Aroclor data set are described below.

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## METHODS FOR ESTIMATING PCB HOMOLOGS FROM AROCLOR DATA

To supplement the congener PCB data set for the sediments, the LWG proposes to include the Aroclor-based data in the modeling of PCB homologs. A straight estimation of homologs from Aroclor quantification is not appropriate for the complex situation in Portland Harbor. Identification of PCB Aroclors at the analytical laboratory can be subjective if the PCB pattern in the sample does not closely reflect the Aroclor standards. This is frequently the case in environmental samples as a result of fate and transport processes, weathering, the presence of more than one Aroclor in a sample, and chromatographic interference. Therefore, in order to estimate homologs from Aroclor data, relationships will be developed based on data from sediment samples for which PCBs were measured using both Aroclor and congener methods. Most likely these relationships will involve using regression techniques to relate concentration or weight percent of each homolog group to Aroclor concentrations (either individual Aroclors or total Aroclors). As part of this effort, an evaluation of whether such relationships vary spatially (i.e., reflecting changing influence of differing sources, transport processes or weathering in different areas of the river) and/or with depth in the sediments. Once developed, these relationship(s) would be used to estimate homolog concentrations as a function of Aroclor concentration, for sample locations having only Aroclor data. (Note for locations having both congener and Aroclor data, the congener data will be used to directly calculate homolog concentrations.)

While not anticipated, it is possible that the relationships between Aroclor and congener/homolog PCBs may not be sufficiently robust to reliably predict homolog concentrations based on Aroclor data. One reason for this is that, although the homolog composition of source Aroclors is relatively well known, the Aroclor-based method for measuring PCBs consists of assigning the resulting chromatogram output to the most closely matching Aroclor compound(s). This provides only an approximation of the true PCB signature of the sample (as discussed above). Therefore, it is possible that differing sources and/or variations in weathering could produce two environmental samples that are quantified as the same Aroclor compound(s) but actually contain very different homolog composition. If no robust relationships between Aroclor and homolog PCBs are found, modeling of PCB homologs will be conducted using only the congener data set. However, before reaching such a

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conclusion, the overall model uncertainty associated with the Aroclor-homolog relationships would need to balanced against the uncertainty associated with using the relatively less dense congener only data for sediment initial conditions. In addition, any presentation of the model-predicted tPCB results will include a clear discussion of the uncertainties associated with the Aroclor-homolog relationships. Significant departures from site-wide correlations and/or model predictions are possible for individual locations. Site-specific decisions based on final modeling results should include consideration of such departures.

We propose to complete the assessment of estimating homologs from Aroclors before conducting the tPCB modeling noted in the first section of this memo. This is the most logical sequence given that the tPCB modeling inputs may vary considerably depending on the outcome of the homolog estimation from Aroclors.